

## NASA Grant NAG3-1437: Final Report

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### Abstract

This report summarizes progress made on NASA Grant NAG3-1437, [“Modeling of Diffusion in Liquid Ge and Its Alloys,”] which was in effect from January 15, 1993 through July 10, 1997. It briefly describes the purpose of the grant, and the work accomplished in simulations and other studies of thermophysical properties of liquid semiconductors and related materials. A list of publications completed with the support of the grant is also given.

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## I. INTRODUCTION.

This is the final report for NASA Grant NAG3-1437, "Modeling of Diffusion in Liquid Ge and its Alloys," which was in effect from January 15, 1993 through July 10, 1997 under the direction of Principal Investigator David G. Stroud, a professor of physics at Ohio State University. Total expenditures for this period, including overhead, amounted to \$154,693.61.

The basic goal of this project has been to develop methods of calculating the self-diffusion coefficient, and related thermophysical properties, of liquid Ge and its alloys as a function of temperature. The work is being done as part of a larger project, under the overall direction of Professor David Matthiasen of Case Western Reserve University, which is aimed at measuring these coefficients in microgravity. The microgravity measurements are expected to be carried out as part of a NASA flight in the next few years. Our role is mainly to provide the theory with which to compare the expected measurements. The various thermophysical quantities are of great fundamental and practical importance, and are needed as inputs to many of the commonly used equations which are thought to govern crystal growth from the melt.

The main results achieved under this grant are described in the publications listed below, to which the interested reader is referred for complete details. A brief summary of the work is given below, in order to put these papers in some perspective. The technical work is still being extended, under a NASA cooperative agreement which is currently in effect at Ohio State. It is expected to continue in the future under a different type of agreement, until the experiment is flown and the results analyzed.

## II. AB INITIO MOLECULAR DYNAMICS SIMULATIONS.

A major effort during the current grant, and an important planned focus of future work, has been to carry out *ab initio* molecular dynamics simulations of self-diffusion coefficients and related thermophysical properties of liquid semiconductors. In this approach, one calculates the total energy of a liquid semiconductor in a particular ionic configuration, using

a version of the local-density functional theory. Then, using a more standard version of molecular dynamics, one moves each ion according to Newton's Laws. The results allow one to calculate a wide range of thermophysical properties, including both electronic and ionic quantities, as a function of temperature and concentration.

In order to develop this program, a graduate student, Rahul Kulkarni, traveled to Berlin, Germany, to obtain an *ab initio* code developed by the electronic structure group of Matthias Scheffler at the University of Berlin. This code was optimized to treat *solid* surfaces (which are much easier to study than liquids). After learning how to use this code, Rahul returned to Columbus and modified it so that it could be applied to liquids. He then proceeded to use it to study self-diffusion and other properties of pure  $\ell$ -Ge and of  $\ell\text{Ge}_x\text{Ga}_{1-x}$ . In the first of these works, he was also assisted by another student, Mr. Wilfried Aulbur. These calculations are, of course, large scale numerical works, even for the 64 atom systems we have treated so far (with periodic boundary conditions, of course).

The first paper based on this approach was published last year (paper no. 5 on the list below). In this paper, we describe the results of *ab initio* molecular dynamics simulations of liquid Ge at five temperatures ranging from 1250 K to 2000 K. The electronic structure is calculated using the local density approximation and generalized norm-conserving pseudopotentials. The calculations yield the pair correlation function, the static structure factor, the bond angle distribution function, the electronic density of states, the atomic self-diffusion coefficient and finally the a. c. conductivity. Near melting, the structure factor has the experimentally observed shoulder on the high- $k$  side of the principal peak, which becomes progressively less distinct at higher temperatures. The bond angle distribution function indicates the persistence of covalent bonding for shorter bond lengths in the liquid state. The electronic density of states is metallic at all the temperatures with a pseudogap at a binding energy of 4.6 eV. The diffusion constant shows a sharp rise between 1250 K and 1500 K ( $1.2 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$  to  $2.0 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$ ), and increases less rapidly at higher temperatures, to only  $2.3 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$  at 2000 K. These results, especially for the conductivity and electronic density of states, are in good agreement with available experiment;

the self-diffusion results, of course, remain to be tested experimentally.

In a second paper using the same code (paper no. 7 below), we extend this work to do *ab initio* molecular dynamics simulations of liquid Ga-Ge alloys at four different concentrations. We use the plane-wave pseudopotential method to carry out the simulations. The physical quantities studied include the partial structure factors, bond-angle distributions, self-diffusion coefficients, electronic density of states and the electrical conductivity. The introduction of Ga causes a distinct reduction of the shoulder in the structure factor of pure  $\ell$ -Ge. Correspondingly, the partial structure factors, pair correlation functions, and bond angle distribution functions all show behavior characteristic of simple liquid metals except at 80% Ge. The electronic density of states shows behavior consistent with the structure: it evolves from having a distinct pseudogap at low concentrations of Ga to being almost free-electron-like for high Ga concentrations. The calculated behaviour of the electrical conductivity agrees qualitatively with previous calculations based on the Faber-Ziman theory of liquid alloys. The self-diffusion coefficients  $D_{Ge-Ge}$  and  $D_{Ga-Ga}$  are consistent with previous calculations and available experiments for the pure liquids. This paper has been accepted for publication in Physical Review B, and will appear in a month or two.

### III. CALCULATIONS USING EMPIRICAL MOLECULAR DYNAMICS TECHNIQUES.

We have also carried out a significant amount of work using so-called empirical molecular dynamics (and Monte Carlo) techniques. In these approaches, instead of calculating the total energy of an alloy from first principles, one uses various types of empirical interatomic (or interionic) interactions, which are obtained by fitting certain properties to experiment. While this approach is, of course, not as desirable as the first-principles techniques, it is complementary, since one can use it to study much larger systems (as large as  $10^7$  for sufficiently simple potentials) than is possible using *ab initio* techniques.

In one recent calculation (paper no. 4 below), we report the results of an extensive

molecular-dynamics study of diffusion in liquid Si and Ge ( $\ell$ -Si and  $\ell$ -Ge) and of impurities in  $\ell$ -Ge, using empirical Stillinger-Weber (SW) potentials with several choices of parameters. We use a numerical algorithm in which the three-body part of the SW potential is decomposed into products of two-body potentials, thereby permitting the study of large systems. One choice of SW parameters agrees very well with the observed  $\ell$ -Ge structure factors. The diffusion coefficients  $D(T)$  at melting are found to be approximately  $6.4 \times 10^{-5}$  cm<sup>2</sup>/sec for  $\ell$ -Si, in good agreement with previous calculations, and about  $4.2 \times 10^{-5}$  and  $4.6 \times 10^{-5}$  cm<sup>2</sup>/sec for two models of  $\ell$ -Ge. In all cases,  $D(T)$  can be fitted to an activated temperature-dependence, with activation energies  $E_d$  of about 0.42 eV for  $\ell$ -Si, and 0.32 or 0.26 eV for two models of  $\ell$ -Ge, as calculated from either the Einstein relation or from a Green-Kubo-type integration of the velocity autocorrelation function.  $D(T)$  for Si impurities in  $\ell$ -Ge, is found to be very similar to the self-diffusion coefficient of  $\ell$ -Ge. We briefly discuss possible reasons why the SW potentials give  $D(T)$ 's substantially lower than *ab initio* predictions.

In another recent paper (no. 6 below), we report the results of a molecular-dynamics study of the surface tension and surface profile of liquid Si and Ge ( $\ell$ -Si and  $\ell$ -Ge) and their alloys, using empirical Stillinger-Weber potentials of the same kind used in paper no. 4). The calculations are carried out at two temperatures slightly above the melting temperatures of Si and Ge, for the pure elements and for the alloys Si<sub>0.8</sub>Ge<sub>0.2</sub> and Si<sub>0.2</sub>Ge<sub>0.8</sub>. They show clear evidence of surface segregation by Ge, the component with the lower surface tension. This calculation is one of the first numerical proofs of this expected behavior, and shows that the empirical molecular-dynamics technique can be used successfully to study the surfaces of liquid mixtures.

In an earlier paper (no. 1 in the list below), we studied the zero-temperature energy and atomic structure of twist grain boundaries (GBs) in diamond (another tetravalent and tetrahedrally coordinated material), using a semi-empirical potential due to Tersoff. The resulting (111) twist GB energies are similar to predictions of an empirical tight-binding potential. For the previously unstudied (001) twist boundaries in diamond, both the energy

and the excess volume are found to be insensitive to misorientation at large twist angles, although small energy cusps exist for the  $\Sigma 5$  GBs. The (001) twist GB energies are typically  $\approx 6J/m^2$ . Significant atomic relaxation occurs only in the two atomic layers nearest the grain boundary. Atoms in these contact layers are predominantly threefold coordinated. For (001) twist GBs, in-plane translations significantly affect the  $\Sigma 5(001)$  energies, but not the high  $\Sigma$  energies.

#### IV. OTHER WORK.

In paper 2 of the list below, by Wang, Stroud and Markworth, we used a simple model to estimate the temperature-dependent thermal conductivity of liquid CdTe, as well as the kinematic viscosity of liquid CdTe and several other liquid semiconductors at melting. Both of these properties are necessary inputs in models of crystal growth from the melt. The thermal conductivity was obtained as the sum of two parts: the ionic contribution  $\kappa_i$ , and the electronic contribution  $\kappa_e$ . The electronic part was obtained from the Wiedemann-Franz law, which connects  $\kappa_e$  to the electrical conductivity  $\sigma$ . The ionic part was obtained from a hard sphere model, as was the kinematic viscosity. The results agree surprisingly well with available experiment.

In paper 3, “A Simple Scaling Formula and Monte Carlo Study...,” by Z. Q. Wang and D. Stroud, we describe a Monte Carlo calculation of the surface tension of nonstoichiometric  $\text{Cd}_x\text{Te}_{1-x}$  alloys, using empirical potentials. The Monte Carlo technique used is similar to one developed in an earlier paper by Wang and Stroud (with NASA support under a predecessor grant). In this case, in order to understand some experimental anomalies (i. e., nonmonotonic variation with concentration) of the surface tension, we use the *same* empirical potentials as were used in the earlier Monte Carlo study of stoichiometric liquid CdTe. Our Monte Carlo calculations do account for the experimental anomaly, which is thus apparently described with sufficient accuracy by our empirical potentials. To shed further light on this anomaly, we also analyze it by means of a scaling formula which requires no

simulations.

In the conference proceeding “Thermophysical Properties of Simple Liquid Metals: A Brief Review of Theory,” Stroud gives an overview of methods for calculating the thermophysical properties of “simple” liquid metals. “Simple” in this case means that the electron-ion interaction is sufficiently weak to be treated by second-order quantum-mechanical perturbation theory. This paper, which was presented at a NASA-sponsored conference, appears in the proceedings of a workshop which was published by NASA.

An overview of our work on semi-empirical methods of calculating surface properties of liquid metals and semiconductors (using Monte Carlo and molecular dynamics simulations, as well as simple scaling arguments) was presented by Wang, Yu, and Stroud at a meeting of the Materials Research Society in Boston this last December. This paper is in press, and will appear as part of a volume of Symposium Proceedings of the Materials Research Society.

Finally, in collaboration with Paul Bristowe, Simon Phillpot, and John Smith, Stroud edited the proceedings of a symposium on Microscopic Simulations of Interfacial Phenomena in Solids and Liquids. This proceedings will appear as a volume in the MRS Proceedings Series (Materials Research Society), early in 1998.

## **V. PERSONNEL.**

A number of scientists have been involved in the work described above; most of these received at least some support from the grant. Besides the Principal Investigator (David G. Stroud), those involved included Dr. Zhiqiang Wang (now at Lucent Technologies in Murray Hill, NJ), Dr. Wenbin Yu (now at Alaris Medical Systems in La Jolla, CA), Dr. Wilfried Aulbur (now a postdoc at the University of California, San Diego), Dr. Alan Markworth and Dr. Suleiman Dregia (both professors in the Department of Materials Science and Engineering at Ohio State University), and Rahul Kulkarni (a current graduate student at Ohio State University).

**VI. PUBLICATIONS SUPPORTED IN WHOLE OR IN PART BY NASA GRANT  
NAG3-1437**

A. Publications in Refereed Journals.

1. "Energy Minimization Studies of Twist Grain Boundaries in Diamond," Z. Q. Wang, S. A. Dregia, and D. Stroud, *Phys. Rev.* **B49**, 8206 (1994).
2. "Thermal Conductivity and Viscosity of Liquid CdTe: A Theoretical Study," Z. Q. Wang, D. Stroud, and A. J. Markworth, *Scripta Metallurgica et Materialia*, vol 30-7, pp. 899-904 (1994).
3. "A Simple Scaling Formula and Monte Carlo Study of Liquid Semiconductor Surfaces: Application to  $\text{Cd}_x\text{Te}_{1-x}$ ," Z. Q. Wang and D. Stroud, *Scripta Metallurgica et Materialia* **32**, pp. 87-92 (1994).
4. "Empirical Molecular Dynamics Study of Diffusion in Liquid Semiconductors," W. Yu, Z. Q. Wang, and D. Stroud, *Phys. Rev.* **B54**, 13946 (1996).
5. "*Ab Initio* Molecular Dynamics Study of Structural and Transport Properties of Liquid Germanium," R. V. Kulkarni, W. G. Aulbur, and D. Stroud, *Phys. Rev.* **B55**, 6896 (1997).
6. "Molecular Dynamics Study of Surface Segregation in Liquid Semiconductor Alloys," Wenbin Yu and D. Stroud, *Phys. Rev.* **B56**, 12243 (1997).
7. "*Ab Initio* Molecular Dynamics Simulation of Liquid  $\text{Ga}_x\text{Ge}_{1-x}$  Alloys," R. V. Kulkarni and D. Stroud, *Phys. Rev. B*, in press (accepted 15 Jan 1998).

B. Publications in Conference Proceedings

1. "Thermophysical Properties of Simple Liquid Metals: A Brief Review of Theory," D. Stroud, in *Workshop on the Thermophysical Properties of Molten Materials*, Proceedings of a Workshop held at NASA Lewis Research Center, October 22 and 23,



1992, ed. T. Overfelt and S. C. Jain (National Aeronautics and Space Administration, Washington, DC, 1993), pp.163-177 (invited paper).

2. "Monte Carlo and Molecular Dynamics Simulations of Liquid Semiconductor Surfaces," Zhiqiang Wang, Wenbin Yu, and David Stroud, to appear in Vol. xx of the Proceedings of the Materials Research Society (1998).

#### C. Books

1. *Microscopic Simulations of Interfacial Phenomena in Solids and Liquids*, edited by Paul D. Bristowe, Simon Phillpot, John R. Smith, and David Stroud, to be published as Vol. xx of the Proceedings of the Materials Research Society, 1998.